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(54) Method for Control of Aldehyde and Unburned Fuel  
Emissions from Alcohol-Fueled Vehicles

(72) Harris, Stephen J.;  
McCabe, Robert W.;  
Mitchell, Patricia J.,  
U.S.A.

(73) Granted to General Motors Corporation  
U.S.A.

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METHOD FOR CONTROL OF ALDEHYDE  
AND UNBURNED FUEL EMISSIONS  
FROM ALCOHOL-FUELED VEHICLES

This invention relates to treatment of exhaust gases from an alcohol-fueled automotive internal combustion engine. More particularly, it relates to reducing alcohol and aldehyde emissions following engine cold start during warm-up.

Reciprocating internal combustion engines in automotive passenger cars and trucks have been operated using an alcohol, such as methyl alcohol or ethyl alcohol, as a fuel. It is known that ethyl alcohol may be substituted as a fuel for gasoline in present vehicle engines with suitable modifications. As the number of alcohol-fueled vehicles increases there may be increased attention given to the emissions they produce.

Ideally, the engine would be operated such that the fuel is burned as completely as possible to carbon dioxide and water without concomitant oxidation of nitrogen. Normally, however, significant amounts of nitrogen oxides ( $\text{NO}_x$ ), carbon monoxide (CO) and unburned or partially oxidized fuel constituents are exhausted from the vehicle. Typically, alcohol-fueled vehicles produce smaller amounts of  $\text{NO}_x$  than their gasoline-fueled counterparts. However, alcohol-fueled engines do produce significant quantities of carbon monoxide and unburned fuel (including aldehydes), particularly during the period of vehicle operation following engine cold start and during engine warm-up. An engine cold start is the common situation in which the vehicle is started when the engine is at ambient temperature. The air-fuel ratio is often too rich



for complete combustion of the fuel. Also, the initially produced exhaust gas is cooled as it passes through the engine exhaust manifold and the exhaust pipe, muffler and tail pipe of the vehicle. Such cooling of the exhaust may impair removal of carbon monoxide or unburned fuel. The engine must operate for a period of a few minutes before it and the exhaust system reach a more or less normal operating temperature and condition.

Exhaust gases from a vehicle engine that contain sufficient oxygen can be brought into contact with an oxidation catalyst to accelerate the oxidation of carbon monoxide and unburned fuel constituents. With gasoline engines, oxidation catalysts have been quite effectively used for this purpose. The active catalytic material has been a small amount of, for example, a noble metal such as platinum and/or palladium. Base metal such as a copper-chromium mixture also has utility. The active catalyst metal is distributed in an extremely thin layer on a high surface area, temperature stable ceramic carrier, such as alumina. The carrier may be in the form of a small pellet or of a small powdered washcoat on a ceramic honeycomb monolith. The pellets or monoliths are housed in a temperature resistant metal converter having an inlet and outlet and located in the exhaust system of the vehicle close to the exhaust manifold.

Such catalysts do not display a high efficiency for conversion of unburned fuel constituents until they have been heated to a threshold or light-off temperature of about 300° C. These catalytic converters are usually heated solely by interaction with the exhaust gas. Depending upon their mass they may require several minutes until they are hot enough for efficient oxidation. Carbon monoxide and unburned

hydrocarbons from gasoline may pass through a cold converter substantially unchanged. The amount of the unwanted emission produced is not increased by the inefficient converter. However, in the case of alcohol  
5 we have found that the cold, inefficient oxidation converter may induce partial oxidation of the unburned fuel to undesirable aldehydes. In other words, in the start-up and warm-up of an alcohol-fueled engine the quantity of unwanted exhaust by-products may actually  
10 be increased when an oxidation converter is employed.

It is an object of this invention to provide a method of treating the flow of unburned fuel constituents from an alcohol-fueled engine during engine warm-up to reduce or minimize the discharge  
15 of unwanted constituents to the atmosphere.

It is a more specific object of this invention to provide a method of using an adsorbent zeolite bed in combination with a suitable oxidation catalyst to reduce the discharge of exhaust emissions from an  
20 alcohol-fueled engine, especially in the period from cold start through engine warm-up. Advantageously, our method may be practiced using a passive system, i.e., it does not require superfluous valves, controls or other means to divert or direct the flow of exhaust  
25 gases.

It is a still further object of the present invention to provide a method of decreasing such exhaust emissions by using an adsorbent bed which will naturally adsorb unburned alcohol and aldehydes  
30 when the exhaust stream is relatively cool and prevent the alcohol and aldehydes from reaching a cold, inefficient oxidation catalyst. Later when the catalyst is hot, the adsorbent bed will release the alcohol and aldehydes to the converter where they are efficiently  
35 oxidized to innocuous by-products.

Brief Summary of the Invention

In accordance with a preferred embodiment of our invention, these and other objects and advantages are accomplished by placing a dual bed converter, containing both a zeolite molecular sieve adsorbent and an oxidation catalyst, in the exhaust system of the alcohol-fueled vehicle. The zeolite bed comprises particles of a suitable aluminosilicate composition having a crystal structure in the form of a three-dimensional cage-like network. The bed can adsorb or trap alcohol and aldehyde molecules from a hot (up to 250° C. to 300° C.) exhaust gas stream. The oxidation catalyst is immediately downstream of the zeolite bed. It promotes the complete oxidation of alcohol or aldehydes in the presence of oxygen when it is at a temperature of about 250° C. to 300° C. or higher.

Following an engine cold start, exhaust gases are pumped from the combustion cylinders by the reciprocating pistons. The gas flows sequentially through the exhaust manifold, an exhaust pipe, the zeolite bed, the oxidation catalyst, and finally out the tail pipe to the atmosphere. At first, these exhaust gases are relatively cool and fuel-rich because the engine and the exhaust system have not been heated to their normal operating state. When the relatively cool gases flow through the zeolite bed, unburned alcohol and any aldehyde by-products are adsorbed in the bed. These constituents do not reach the then ineffective oxidation catalyst. The major portion of the exhaust stream comprising nitrogen, carbon monoxide, carbon dioxide and the like, flows through the oxidation converter and out the tail pipe. They commence heating of the converter as they flow.

The temperature of the exhaust gas stream reaching the adsorbent bed and catalyst continues to increase during the first couple of minutes of engine operation, but alcohol and aldehyde constituents are trapped and held in the zeolite bed. As the exhaust gas heats or interacts with the catalyst to heat it to a temperature approaching, for example 300° C., the zeolite bed is also warmed and begins to give up or release the alcohol and aldehydes. At this point the catalytic converter is capable of efficiently promoting the oxidation of these materials fully to carbon dioxide and water. The discharge of aldehyde or other partially oxidized alcohol by-products to the atmosphere is reduced or minimized.

Further operation of the engine and exhaust system at normal operating temperature, purges or regenerates the zeolite bed of adsorbed exhaust emissions. This soon restores its capacity to repeat its storage function following a subsequent cold start. The catalytic converter continues to perform its oxidation function. The zeolite is thermally stable at normal exhaust temperatures and the adsorbent bed need not be by-passed during normal engine operation.

Thus, by using a zeolite adsorbent bed in an exhaust system containing an oxidation converter, the system will naturally hold back unburned alcohol during engine start-up and release it at normal engine operation. In a particularly convenient embodiment a known dual bed downflow catalytic converter structure can be employed in which zeolite particles constitute the upper bed and oxidation catalyst pellets make up the lower bed.

In one embodiment of our invention it may also be useful to add a suitable quantity of secondary air to the exhaust stream, upstream of the zeolite

bed. This practice and its advantages will be described in more detail below.

Our method will be better understood in view of a detailed description thereof in which  
5 reference will be made to the drawing in which the single Figure of the drawing is a schematic flow diagram depicting our method.

#### Detailed Description of the Invention

We have tested and demonstrated the practice  
10 of our method on an ethanol-fueled Brazilian made automobile (by GM do Brasil), an Opala Commodoro. The vehicle was equipped with a 2.5 L displacement engine, a four-speed manual transmission and manual  
15 choke. The vehicle was used to perform emission tests and was then operated on a chassis dynamometer. The car was operated following the eighteen specific cycles prescribed by the 1978 United States Federal Test Procedure (FTP). Provision was made to operate  
20 the manual choke and manual transmission during the eighteen cycles of the procedure. The first five cycles were in the cold start phase and thirteen cycles were in the stabilized phase.

A 250 cubic inch total capacity dual bed  
25 downflow catalytic converter was installed in the vehicle's exhaust system just under the floor of the front passenger compartment. The exhaust stream flow path was like that shown in the Figure of the drawing. All of the exhaust gases emanating from the engine flowed through the converter and then out the tail  
30 pipe to the atmosphere. Provision was made for sampling exhaust gases at the exhaust manifold and the end of the tail pipe. However, no provision was made to inject secondary air and no other modifications were made in this exhaust system. The top half  
35 (125 cubic inches) of the dual bed was filled with

Union Carbide Corporation's Linde 13X\*type zeolite molecular sieve pellets. The lower half of the dual bed converter was filled with oxidation catalyst pellets. We have conducted tests using 3 mm diameter alumina beads impregnated with platinum and palladium (Pt-Pd catalyst). We have also conducted tests with hopcalite catalyst particles. The Pt-Pd catalyst was a commercial oxidizing catalyst for exhaust emissions. It contained 0.054 weight percent Pt and 0.022 weight percent Pd. The hopcalite catalyst was a mixture of copper and manganese oxides obtained from Mine Safety Appliances Company.

The converter size and location was similar to those used on comparable United States gasoline-fueled vehicles but no attempt was made to determine whether the size or location was optimal.

For purposes of comparison, like tests were also conducted with the same car using a single bed catalytic converter containing no zeolite adsorbent but filled with 160 cubic inches of oxidation catalyst. While these tests were intended to provide a comparison of the effect of the oxidizing converter on engine operation without the use of the adsorbent bed, it is to be noted that the amount of oxidizing catalyst was greater in this instance.

The fuel was a blend of 6 volume percent (7.6 weight percent) water in absolute (undenatured) ethyl alcohol. This mixture was selected to approximate the composition of a normally pure ethanol fuel.

The following observations were made from analysis of the engine-out emissions and the tail pipe emissions by operating the alcohol-fueled vehicle in three different modes: (1) without modification (i.e., no catalytic converter or adsorbent bed); (2) with only a catalytic converter in the exhaust

\*trademark

system; and (3) with the dual bed zeolite adsorbent-oxidation catalyst. In our evaluation of our method we focussed on aldehyde emissions.

As would be expected, the use of an oxidation catalyst alone (as compared to no emission control at all) is not effective in reducing aldehyde emissions immediately following cold start or for much of the engine warm-up period. In fact, some oxidation catalysts, such as a copper-chromium oxidation catalyst, will actually substantially increase aldehyde emissions during this period. This is apparently because the catalyst is effective in initiating some oxidation, converting the ethanol to acetaldehyde, but is not effective to complete the oxidation to carbon dioxide and water. It was soon realized that aldehyde emissions from an alcohol-fueled engine could not readily be controlled during engine warm-up by simply adding an oxidation catalyst. In operating the vehicle described we found that the 160 cubic inch hopcalite catalyst bed alone reduced aldehyde emissions over the full eighteen-cycle FTP procedure about 59% when compared to aldehyde emissions from the vehicle operated without any exhaust control. Of course, this full procedure included five cycles of cold engine start and warm-up, plus thirteen cycles of stabilized operation. On the same basis, the Pt-Pd catalyst alone reduced aldehyde emissions about 70%.

Much of the aldehyde emissions that escaped the tail pipe were generated during the first five cycles of the FTP.

A significant improvement was obtained when the tests were repeated using the dual bed downflow

converter. In one instance it contained a Linde 13X zeolite upper bed and hopcalite catalyst lower bed and in the other instance it contained an upper bed of 13X zeolite and a lower bed of Pt-Pd. Aldehyde emissions with the zeolite and hopcalite dual bed were only 70% of those with the hopcalite alone. Aldehyde emissions with the Pt-Pd catalyst and zeolite were 53% of those with the Pt-Pd catalyst alone.

During the FTP cycle runs the manual choke is partially closed through three of the five cycles during engine warm-up following cold start. This, of course, means that the engine runs rich and that the exhaust gas probably does not contain sufficient oxygen to complete the oxidation of unburned alcohol. For this reason it may be desirable in some practices of our method to employ a conventional air pump to inject secondary air into the exhaust stream, just upstream of the zeolite bed. A suitable point of injection of this secondary air stream is indicated by the dotted line in the Figure of the drawing. This air stream would serve several useful purposes. It would assure that there would be sufficient oxygen in the exhaust stream at all times to complete the oxidation of all unburned emission constituents reaching an operating oxidation catalyst. It also would reduce the temperature of the exhaust stream entering the zeolite bed and thus delay the time at which adsorbed alcohol is purged from the bed. At the same time, the oxygen and carbon monoxide flowing through the zeolite bed to the oxidation catalyst would tend to raise its temperature by undergoing exothermic reaction, and thus shorten the period from cold start until the catalyst is at its effective temperature.

We have also shown the effectiveness of our method in a laboratory reactor. We formed a dual bed of Linde 13X molecular sieve and hopcalite catalyst in a tube furnace. We formed a synthetic exhaust stream consisting of 1,000 ppm ethanol and 1% oxygen in nitrogen and passed it through the dual bed. At the same time, we started heating the tube furnace from ambient temperature to 350° C. We were able to heat to that temperature and maintain that temperature without the observation of ethanol or acetaldehyde in the reactor effluent. The only carbon-containing products observed in the reactor effluent were carbon dioxide and a small amount of ethylene. Small amounts of ethylene are formed on the molecular sieve from the dehydration of ethanol.

It is the cooperation between the zeolite molecular sieve and the oxidation catalyst that is the basis of our passive exhaust treatment method. The former works (adsorbs) while the latter is warming up. When the catalyst is operative, the adsorption bed is regenerating itself. Of course, the zeolite is only needed because known, effective and durable oxidation catalysts are not fully operative until they are hot. The selection of a particular oxidation catalyst is not a critical aspect of our invention.

The oxidation catalyst presently commonly used consists of platinum or mixtures of platinum and other noble metals, notably palladium. As stated, they are commonly used as coatings on alumina pellets or heads or on ceramic monolithic honeycombs. Other oxidation catalyst compositions include copper-chromium (for example,  $\text{CuO} \cdot \text{CuCr}_2\text{O}_4$ ) and hopcalite (a typical mixture consists of 60%  $\text{MnO}_2$  and 40%  $\text{CuO}$ ). In addition, there are a large number of other metal oxide-containing materials that are effective to some degree as oxidation catalysts.

There are mineral zeolites and synthetic zeolites. In general, they are crystalline aluminosilicates high in silica. They usually contain a cation such as sodium, potassium, ammonium, calcium, barium or the like. It is known by X-ray crystal structure analysis that many of them have framework, crystal structures that are sieve-like on a molecular scale. They have known utility for carrying out operations by selective adsorption of molecules.

We used a commercially available synthetic zeolite, a faujasite type framework structure -- Zeolite 13X\*. The material was obtained from Union Carbide Corporation. The typical unit cell contents of Zeolite 13X\* are  $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 264\text{H}_2\text{O}$ . This material is known to be capable of adsorbing molecules as large as tributylamine under suitable conditions.

We considered Zeolite 13X\* suitable for use in our method with the engine and oxidation catalyst employed. However, we view that use as merely illustrative and do not intend to be limited to this particular form of zeolite. Other zeolites, including other X-type zeolites, may be preferred in other engine oxidation catalyst combinations.

As noted above, an important feature of our method is that the combination of the zeolite bed and oxidation catalyst can function passively. Aldehyde and alcohol emissions to the atmosphere can be decreased simply by directing the engine exhaust gas stream sequentially through the two beds. The beds do not have to be heated or cooled apart from their natural interaction with the exhaust stream. In the preferred mode of practicing the invention, no provision has to be made for bypassing the catalyst bed during engine warm-up or for bypassing the zeolite bed when the

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\* trademark

exhaust is hot. No special purge stream (other than exhaust gas) need be used to remove adsorbed alcohol or aldehyde from the zeolite and thus restore or regenerate its adsorbent capacity for the next time the engine is started cold. Of course, as we have stated, it may be useful to inject air into the exhaust stream before it reaches the dual bed converter or before it reaches the catalyst bed. However, this is for the purpose of assuring there is sufficient oxygen in the exhaust stream to complete the combustion of the emissions. This practice is known. When using it, it is for the purpose of improving the results of our method but it is not necessary to the practice of the method.

We know of no other adsorbent material that can be used in place of the zeolite in the practice of our method. While there are many other known adsorbent materials, none so far as we know will trap and hold aldehydes and unburned alcohols from a hot exhaust stream until an oxidation catalyst has been heated to its light-off temperature.

While our invention has been disclosed in terms of a preferred embodiment thereof, it will be appreciated that other forms could readily be adapted by one skilled in the art. Accordingly, our invention is to be limited only by the scope of the following claims.

The embodiments of the invention in which an exclusive property of privilege is claimed are defined as follows:

1. The method of reducing exhaust emissions from an alcohol-fueled automotive vehicle during engine cold start and warm-up, comprising

5 directing the initially relatively cool engine start-up exhaust gas through a bed of zeolite particles and then over an oxidation catalyst before the gas is discharged to the atmosphere, said zeolite adsorbing unburned or incompletely burned alcohol from the exhaust stream and the exhaust gas then commencing  
10 heating of the catalyst to its effective operating temperature.

continuing to pass progressively warmer exhaust gas through said bed and over said catalyst, the bed continuing to adsorb alcohol or its partially  
15 oxidized by-products and the catalyst continuing to be heated by the exhaust gases, and

further continuing such passage of exhaust gas at a temperature sufficient to remove adsorbed alcohol and by-products from said bed and to carry  
20 them to the catalyst where effective oxidation is promoted.

2. The method of reducing exhaust emissions from an alcohol-fueled automotive vehicle during engine cold start and warm-up, comprising passing the exhaust gas from the time of engine start and continually  
5 thereafter through a bed of zeolite adsorbent material and then into contact with an initially unheated oxidation catalyst before the gas is discharged to the atmosphere, whereby, at first, aldehyde and unburned alcohol constituents in the exhaust gas  
10 are adsorbed on the zeolite where they are temporarily

stored and prevented from raw discharge to the atmosphere, the continuing flow of zeolite-contacted exhaust gas then gradually heating the oxidation catalyst to a temperature region in which it can  
15 effectively promote the oxidation of such constituents, the zeolite continuing to adsorb and store such constituents until it is heated by the exhaust to approximately the operating temperature of the catalyst whereupon it releases adsorbed constituents  
20 back to flowing exhaust gas in which they are carried to the catalyst and burned before discharge to the atmosphere, the removal of the constituents from the zeolite restoring its capacity to again adsorb like constituents from a cold start engine exhaust.

3. The method of reducing exhaust emissions from an alcohol-fueled automotive vehicle during engine cold start and warm-up, comprising

directing the initially relatively cool  
5 engine start-up exhaust gas through a bed of zeolite particles and then over an oxidation catalyst before the gas is discharged to the atmosphere, said zeolite adsorbing unburned or incompletely burned alcohol from the exhaust stream and the exhaust gas then commencing  
10 heating of the catalyst to its effective operating temperature,

continuing to pass progressively warmer exhaust gas through said bed and over said catalyst, the bed continuing to adsorb alcohol or its partially  
15 oxidized by-products and the catalyst continuing to be heated by the exhaust gases,

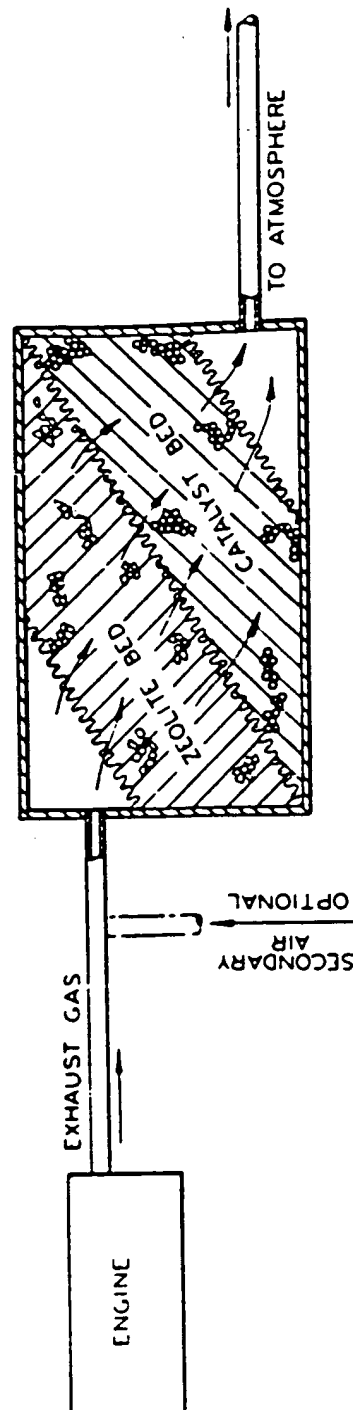
further continuing such passage of exhaust gas at a temperature sufficient to remove adsorbed alcohol and by-products from said bed and to carry them  
20 to the catalyst, and

15

adding air to the exhaust gas stream  
before it reaches the catalyst if necessary to  
provide sufficient oxygen in the stream for effi-  
cient oxidation of removed constituents to carbon  
25 dioxide and water.

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*Goetting & Henderson*